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Modified zeolitic imidazolate framework-8 as solid-phase  
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1    **Modified zeolitic imidazolate framework-8 as solid-phase microextraction Arrow coating for**  
2    **sampling of amines in wastewater and food samples followed by gas chromatography-mass**  
3    **spectrometry**

4

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## 13    **Abstract**

14        In this study, a novel solid phase microextraction (SPME) Arrow was prepared for the sampling of  
15    volatile low molecular weight alkylamines (trimethylamine (TMA) and triethylamine (TEA)) in  
16    wastewater, salmon and mushroom samples before gas chromatographic separation with mass  
17    spectrometer as detector. Acidified zeolitic imidazolate framework-8 (A-ZIF-8) was utilized as  
18    adsorbent and poly(vinyl chloride) (PVC) as the adhesive. The custom SPME Arrow was fabricated  
19    via a physical adhesion: (1) ZIF-8 particles were suspended in a mixture of tetrahydrofuran (THF)  
20    and PVC to form a homogeneous suspension, (2) a non-coated stainless steel SPME Arrow was  
21    dipped in the ZIF-8/PVC suspension for several times to obtain a uniform and thick coating, (3) the  
22    pore size of ZIF-8 was modified by headspace exposure to hydrochloric acid in order to increase the  
23    extraction efficiency for amines. The effect of ZIF-8 concentration in PVC solution, dipping cycles  
24    and aging temperature on extraction efficiency was investigated. In addition, sampling parameters  
25    such as NaCl concentration, sample volume, extraction time, potassium hydroxide concentration,  
26    desorption temperature and desorption time were optimized. The Arrow-to-Arrow reproducibilities  
27    (RSDs) for five ZIF-8 coated Arrows were 15.6% and 13.3% for TMA and TEA, respectively. The  
28    extraction with A-ZIF-8/PVC Arrow was highly reproducible for at least 130 cycles without  
29    noticeable decrease of performance (RSD<12.5%). Headspace SPME of 7.5 mL sample solution with  
30    the fabricated ZIF-8 coated Arrow achieved linear ranges of 1-200 ng mL<sup>-1</sup> for both TMA and TEA.  
31    The limit of quantitation (LOQ) was 1 ng mL<sup>-1</sup> for both TMA and TEA. The method was successfully  
32    applied to the determination of TMA and TEA in wastewater, salmon and mushroom samples giving  
33    satisfactory selectivity towards the studied amines.

34

35    **Keywords:** Acidified Zeolitic Imidazolate Framework-8; Amines; Food; Gas Chromatography-Mass  
36    Spectrometry; Solid Phase Microextraction Arrow; Wastewater

## 37 1. Introduction

38 Solid phase microextraction (SPME) was introduced by Pawliszyn and his co-workers in 1990s.[1]  
39 It is a simple, time-saving, environmentally friendly and solventless non-exhaustive sampling  
40 technique, which integrates sampling and sample preparation in one step.[2] Conventional SPME  
41 fiber comprises of a fused silica fiber wrapped with the sorbent material, such as  
42 polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), carbowax (CW), carboxen  
43 (CAR), polyethylene glycol (PEG), templated resin (CW/TPR) and their composite materials.[3] In  
44 the last two decades, SPME has been extensively used for the determination of volatile, semi-volatile  
45 and non-volatile, nonpolar and polar compounds in environmental,[2] biogenic [4] and food [5-7]  
46 samples with both headspace (HS) and direct insertion extraction (DI-SPME) modes.

47 SPME Arrow is a recent development of SPME and has been successfully exploited in the  
48 determination of amines and polycyclic aromatic hydrocarbons (PAHs.) [8, 9] There are already many  
49 coatings commercially available for SPME Arrow such as PDMS/Carboxen-1000, PDMS/Carboxen-  
50 WR and PDMS. SPME Arrow has large sorbent volume, which increases sample capacity and  
51 efficiency of the extraction. Moreover, its design makes it resistant during manipulation and less  
52 likely to core the inlet septum in gas chromatograph.

53 In recent decades, amines as widespread pollutant compounds in the environment have drawn  
54 extensive scientific, societal and political attention due to their toxic, carcinogenic and  
55 bioaccumulation characteristics.[10] Moreover, their importance in atmospheric chemistry and effect  
56 on global climate has been shown.[11] Because of the increasing use in human activities, such as  
57 farming and industry, amines should be monitored, especially in densely populated areas. In addition,  
58 amines are good food safety markers, especially for fish.[12] Thus, sensitive method for their  
59 determination in biological matrices is needed. Unfortunately amines are challenging compounds to

60 be analyzed due to their volatility and high polarity, which make them difficult to separate from  
61 sample matrices.

62 Amines have been analyzed in environmental [13-16], biological [17] and food [18-21] samples  
63 using a variety of sampling techniques, such as: SPME [15-17, 22], liquid–liquid–liquid  
64 microextraction (LLLME) [13, 14, 18], solid phase extraction (SPE) [19-21] and many analytical  
65 techniques including gas chromatography (GC) coupled with different detectors, high performance  
66 liquid chromatography (HPLC) and capillary electrophoresis (CE) [23]. SPME has been recognized  
67 as the extraction method of choice in a wide variety of analyses with different sample matrices, and  
68 GC-MS has been commonly used in the analysis of volatile amines due to its simplicity, good  
69 sensitivity and relatively short analysis time. In our previous work, a series of SPME fibers and SPME  
70 Arrows with various coating materials were employed for the HS-SPME of dimethylamine and  
71 trimethylamine that were analyzed by GC-MS.[8] Carbon-based porous particle material, Carboxen-  
72 1000 with a pore size around 1 nm exhibited the best extraction capacity to these two amines in HS-  
73 SPME mode for air and wastewater samples. The results achieved encouraged us to evaluate further  
74 the performance of other porous materials for the extraction of volatile amines.

75 Metal organic frameworks (MOFs) have been widely utilized due to their attractive properties such  
76 as the possibility of pore size modification, large surface area, micro-porosity, and good thermal  
77 stability.[24-26] However, many MOFs are very sensitive to water as their metal-oxygen bonds can  
78 easily be degraded by even a small amount of moisture.[25] Zeolite imidazolate frameworks (ZIFs)  
79 are a relatively new class of water-stable frameworks and they have been utilized for pre-treatment  
80 of aqueous sample because of stronger metal-ligand bonds and hydrophobicity.[26] ZIF-8 has become  
81 one of the most studied ZIF materials because it does not only possess the MOFs original properties  
82 but also has exceptional thermal and chemical stability in both water and alkaline solutions.[27] All  
83 of the advantages mentioned above attracted us to investigate the potential application of ZIF-8 as a  
84 high-efficiency sorbent for the extraction and preconcentration of analytes from the aqueous phase.

85 In this study our goal was to develop a new hydrophobic ZIF-8 based SPME Arrow using PVC as  
86 adhesive with dipping method. To increase the extraction capacity of volatile amines, the pore size  
87 of ZIF-8 was modified by hydrochloric acid. The acidified-ZIF-8 SPME Arrow together with GC-  
88 MS analysis was evaluated for the determination of trimethylamine (TMA) and triethylamine (TEA)  
89 in wastewater, salmon and mushroom samples. The results were compared with those achieved with  
90 a previously optimized method based on PDMS/Carboxen-1000 Arrow.

## 91 **2. Experimental**

### 92 **2.1. Chemicals and materials**

93 Trichloroacetic acid ( $\geq 99.5\%$ ), tetrahydrofuran (THF) ( $\geq 99.9\%$ ), methanol ( $\geq 99.9\%$ ), zeolitic  
94 imidazolate framework-8 (ZIF-8), poly(vinyl chloride) (PVC), trimethylamine hydrochloride  
95 ( $\text{TMA} \cdot \text{HCl}$ , 98%) and triethylamine hydrochloride ( $\text{TEA} \cdot \text{HCl}$ ,  $\geq 99.0\%$ ) were purchased from Sigma-  
96 Aldrich (St. Louis, USA). Sodium chloride ( $\text{NaCl}$ ) was purchased from Fisher Scientific  
97 (Loughborough, Leics, UK). Hydrochloric acid ( $\text{HCl}$ ) (both 0.1 and 1 M) and sodium hydroxide  
98 ( $\text{NaOH}$ ) (0.1 M) were purchased from Oy FF-Chemicals Ab (Haukipudas, Finland). Potassium  
99 hydroxide ( $\text{KOH}$ ) was purchased from VWR Chemicals (Pennsylvania, USA). Perchloric acid  
100 ( $\text{HClO}_4$ ) was from Merck (Darmstadt, Germany). Ultrapure water from the water purification system  
101 (Millipore DirectQ-UV, Billerica, MA, USA) was used for stock, standard, and sample solution  
102 preparation. Individual stock solutions of TMA and TEA were prepared in ultrapure water at a  
103 concentration of  $1000 \text{ mg L}^{-1}$  and stored at  $4^\circ\text{C}$  in the refrigerator.

104

### 105 **2.2. Preparation of ZIF-8/PVC coated SPME Arrow**

106 The ZIF-8 solution was prepared as follows: 1 mL of THF was added into a 2 mL plastic tube, then  
107 10 mg of PVC was added and the mixture was shaken on an IKA Electronic VIBRAX-VXR shaker  
108 (Breslau, Germany) 1200 rpm for 10 min. 60 mg of ZIF-8 particles were then added to the mixture

109 and shaken at 1200 rpm for 15 minutes. Finally, a viscous white ZIF-8/PVC/THF suspension was  
110 obtained.

111 The preparation schematic of ZIF-8 coated Arrow is shown in Figure 1. An uncoated SPME Arrow  
112 was first washed by sonication in 10 mL methanol, followed by 10 mL NaOH (15 minutes each) and  
113 rinsed three times with ultrapure water. Then, Arrow was etched by immersion into 10 mL of 0.1 M  
114 HCl for 1 hour in order to increase the Arrow surface area. After that, Arrow was washed three times  
115 with ultrapure water and dried at room temperature.

116 The etched Arrow was immersed into ZIF-8/PVC/THF suspension for 10 seconds and pulled out  
117 slowly during several seconds. Then Arrow was heated to 200 °C in an oven for 15 minutes to remove  
118 THF. This cycle was repeated up to five times.

119 Aging of the ZIF-8/PVC Arrow was carried out in the GC injection port with helium (99.996%,  
120 AGA, Espoo, Finland) as the carrier gas in order to eliminate reduced residual impurities. The  
121 temperature was 250 °C and the aging time was 60 minutes.

122 Finally, the aged ZIF-8/PVC Arrow was exposed for 1 hour to 10 mL of 1 M HCl solution in a 20  
123 mL headspace vial equipped with a PTFE/silicone septum screw-cap. Then vial was heated to 50 °C  
124 in a heating block. Headspace acidification was chosen to avoid possible decomposition of ZIF-8.  
125 The HCl exposed ZIF-8/PVC (A-ZIF-8/PVC) Arrow was dried in the 200 °C oven for 30 minutes in  
126 order to remove HCl.

127 A ZIF-8/PVC Arrow without HCl exposure, a pure PVC Arrow and a pure ZIF-8 Arrow were also  
128 prepared for comparison.

129 Before each sampling, the SPME Arrows were pre-conditioned in the GC injection port at 250 °C  
130 for 15 minutes.

131 **Figure 1.**

### 132    **2.3. Instruments and GC-MS analysis**

133        The surface morphology of the A-ZIF-8/PVC coated SPME Arrow was studied by scanning  
134    electron microscopy (SEM) (Hitachi, model S-4800, Japan). The surface area, pore size, and pore  
135    volumes were determined by nitrogen physisorption measurements at 77 K (ASAP 2010,  
136    Micromeritics Co., Norcross, GA, USA). The X-ray photoelectron spectroscopy (XPS) spectra of the  
137    ZIF-8 coating were obtained with a PHI Quantum 2000 instrument (Physical Electronics, Inc.,  
138    Chanhassen, MN, USA).

139        The GC-MS analysis was carried out using an Agilent 6890 N gas chromatograph coupled with  
140    an Agilent 5973 C mass selective detector or with an Agilent 5975 C mass selective detector (Agilent  
141    Technologies, Palo Alto, USA). The former mass selective detector was mainly used in coating  
142    preparation optimization and the latter one in SPME conditions optimization, method validation, and  
143    natural sample analysis. An InertCap for Amines capillary column (30 m length  $\times$  0.25 mm i.d., GL  
144    Sciences, Tokyo, Japan) was used for the chromatographic separation. The instrumental conditions  
145    of GC-MS for analysis of amines were as follows: injector temperature, 270 °C; transfer line  
146    temperature, 250 °C; ion source temperature, 230 °C; quadrupole temperature, 150 °C; oven  
147    temperature program: 40 °C (held for 5 minutes) and then increased to 250 °C at a rate of 30 °C min<sup>-1</sup>  
148    (held for 4 minutes). The mass spectrometer was operated in the electron ionization (EI) mode (70  
149    eV). Data acquisition was carried out in scan mode in m/z range of 30-300. Helium (99.996% purity,  
150    AGA, Espoo, Finland) was used as carrier gas at a constant flow rate of 1.2 mL min<sup>-1</sup>.

151        Uncoated solid phase microextraction Arrows (for coating length of 20 mm), PDMS/Carboxen-  
152    1000 Arrows (sorbent film thickness 120  $\mu$ m and the sorbent length 20 mm) and PAL RTC auto-  
153    sampler were kindly provided by CTC Analytics AG (Zwingen, Switzerland).

### 154    **2.4. SPME procedures**



155 The preliminary optimization of coating preparation and SPME sampling conditions with A-ZIF-  
156 8/PVC coated Arrow analysis was carried out manually. The final optimization was performed using  
157 the CTC autosampler. The general SPME procedure was as follows: diluted amine standard solution,  
158 a stir bar (10 mm × 3 mm) and solid NaCl were added into a 20 mL headspace vial equipped with a  
159 PTFE/silicone septum screw-cap (both from Phenomenex, Torrance, California, USA). 500 µL KOH  
160 solution was then injected into the headspace vial by a 500 µL syringe in order to release the amines  
161 into the headspace. The extraction was done by puncturing the septum with the SPME Arrow and  
162 exposing the sorbent to headspace inside the vial.

163 The sample solution preparation and desorption procedures of automated sampling were the same  
164 to that of manual sampling given above. The difference of automatic sampling was the incubation  
165 temperature, which was 40 °C (5 min). The extraction was carried out at 40 °C, which was the  
166 minimum value for the sampler system.

167 PDMS/Carboxen-1000 Arrow was selected for the comparison with A-ZIF-8/PVC coated Arrow  
168 because of its higher extraction capacity for amines compared to other commercial SPME Arrows  
169 and SPME fibers. The optimal SPME conditions were the same as described in our previous study  
170 with small modifications.[8] For extraction, 5 mL sample solution, 2 g NaCl and 250 µL 5 M KOH  
171 were mixed, and then incubated for 10 min at room temperature. For desorption, 40 seconds at 250  
172 °C was used. Extraction times were optimized due to the use of an autosampler. Extraction was carried  
173 out at 40 °C.

174 The pre-condition time between the extractions was 10 min for both A-ZIF-8/PVC coated Arrow  
175 and commercial PDMS/Carboxen-1000 Arrow.

## 176 **2.5. Natural sample applications**

### 177 **2.5.1. Wastewater sample analysis**

178 Influent and effluent wastewater samples were from Viikinmäki municipal wastewater treatment  
179 plant (WWTP), which is located in Helsinki, Finland. The samples were collected into pre-cleaned  
180 plastic bottles and stored in the refrigerator at 4 °C prior to analysis. To assess recovery with A-ZIF-  
181 8/PVC SPME Arrow, influent wastewater samples (7.5 mL) were spiked with 75 and 150 µL of TMA  
182 and TEA standard solution (10 mg L<sup>-1</sup>), respectively. For PDMS/Carboxen-1000 SPME Arrow  
183 recovery, influent samples (5.0 mL) were spiked with 50 and 100 µL of TMA and TEA standard  
184 solution (10 mg L<sup>-1</sup>), respectively. The spiking resulted in 100 ng mL<sup>-1</sup> (TMA) and 200 ng mL<sup>-1</sup> (TEA)  
185 with both sample volumes.

### 186 **2.5.2. Fish sample analysis**

187 The salmon sample was purchased from a local supermarket in Helsinki, Finland. The sample was  
188 stored at room temperature for 0, 1, 2, 3 and 4 days in order to monitor changes in the amine  
189 concentrations. On the first day (day 0), the fish sample was analyzed immediately without storage.  
190 The sample preparation was performed as follows: 50 mL 0.4 M HClO<sub>4</sub> was added to approximately  
191 10 g of fish and the mixture was homogenized in a 1000 mL plastic graduated cylinder (Bosch,  
192 Gerlingen, Germany) with a kitchen blender at maximum power for 5 minutes. The homogenate was  
193 transferred into a 100 mL volumetric flask and the plastic graduated cylinder was washed with 10 mL  
194 of HClO<sub>4</sub> three times and washing solutions were added into the flask. Finally, the volume of the  
195 mixture was then adjusted to 100 mL with 0.4 M HClO<sub>4</sub>.

### 196 **2.5.3. Mushroom sample analysis**

197 Four types of fruiting bodies (wood-decay fungus, Supplement Figure S1) were collected from a  
198 forest near Kumpula Campus of the University of Helsinki (Helsinki, Finland) on the 1<sup>st</sup> of  
199 September, 2016 and stored overnight at +4 °C. The following day they were cut into cubes with  
200 diameters of roughly 1 cm. Approximately 4 grams of each sample was weighed into 50 mL Falcon  
201 tube and 15 mL of 10% (w/v) TCA was added. Samples were homogenized with an IKA Ultra Turrax

202 homogenizer for 2 minutes at maximum speed and centrifuged. The supernatant was moved to a 50  
203 mL volumetric flask, followed by a second homogenization of the fish in 15 mL of 10% (w/v) TCA  
204 and centrifugation. The supernatant was combined with the previous one and the volume of the extract  
205 was adjusted to 50 mL with 10% (w/v) TCA.

## 206 **3. Results and discussion.**

### 207 **3.1. Acidification of ZIF-8 coated SPME Arrow**

208 An SPME Arrow coated only with ZIF-8 was first prepared in order to investigate its extraction  
209 efficiency towards TMA. ZIF-8 exhibited considerably lower extraction efficiencies than  
210 PDMS/Carboxen-1000 Arrow as shown in Figure 2a, most probably due to the pore size of ZIF-8  
211 (5.6 Å), which is smaller than the molecular size of TMA (approximately 8.4 Å)[28, 29]. This  
212 prevents effective capture of the TMA molecule to the sorbent.

#### 213 **Figure 2.**

214 ZIF-8 is sensitive to acid and its pore size can be enlarged [30]. ZIF-8 particles decompose very  
215 quickly if immersed into an acid solution directly. Thus, in order to minimize the degradation, we  
216 exposed ZIF-8 to a 1 M water solution of HCl in the headspace. The elemental compositions of the  
217 ZIF-8 particle coatings were compared by XPS before and after the acid exposure (data not shown).  
218 The composition of ZIF-8 particle appeared to be unchanged. Moreover, the pore size of ZIF-8  
219 particles before and after acidification was characterized by nitrogen physisorption measurements.  
220 The results indicated that before acidification the pore size of ZIF-8 particles matched the results  
221 reported in the literature[29], but after the acidification, the pore size increased to about 50 nm. The  
222 results from XPS and nitrogen sorption characterizations proved that headspace acidification strategy  
223 was capable of changing the pore size of ZIF-8 particles without changing its elemental composition.

224 As shown in Figure 2a, the extraction performance of the acid exposed ZIF-8 coated Arrow  
225 increased 1290 % in peak area compared to the non-exposed ZIF-8 Arrow, but it was still lower than

that of PDMS/Carboxen-1000 Arrow. Moreover, the stability of the ZIF-8 coating on the surface of the Arrow was poor and it was visibly damaged after only five extraction/desorption cycles. Accordingly an adhesive was needed for the preparation of a stable SPME Arrow coating. PVC was selected because it is a relatively heat-resistant polymer which can be easily dissolved in THF and reassembled after THF removal. The acid exposed ZIF-8/PVC Arrow and non-exposed ZIF-8/PVC Arrow were compared for the extraction of TMA. Due to the increased thickness of ZIF-8 (from around 5  $\mu\text{m}$  to 70  $\mu\text{m}$ ), both Arrows showed increased extraction capacity. The increase in extraction performance after acid exposure was similar to non-PVC Arrow, 1049%. A PVC coated SPME Arrow (PVC-SPME Arrow) was prepared and tested under the same extraction and desorption conditions as ZIF-8/PVC SPME Arrow, and it did not show any extraction capability towards TMA (data not shown). Thus, it could be concluded that the extraction of TMA was caused by the acidified-ZIF-8 sorbent. By comparing acidified-ZIF-8/PVC SPME Arrow with PDMS/Carboxen-1000 SPME Arrow in Figures 2a and 2b, the extraction performance of former Arrow was 331% greater than the latter Arrow even though the coating thickness was lower (70  $\mu\text{m}$  for A-ZIF-8/PVC Arrow and 120  $\mu\text{m}$  for PDMS/Carboxen-1000).

### 3.2. Optimization of ZIF-8 coating preparation procedure

It was important to optimize the preparation of the SPME Arrow coating for the best performance. Several parameters including adhesive to sorbent ratio, number of dipping cycles, and an aging temperature were optimized. The adhesive to sorbent ratio influences the extraction performance by the amount of sorbent that has been immobilized on the Arrow surface. Four A-ZIF-8/PVC Arrows were prepared in different ZIF-8 to PVC mass ratios: 4:1, 6:1, 8:1 and 10:1. All of them were prepared in 2 mL tubes with 1 mL THF so that 20 mm long Arrow carrier could be dipped in preparation solution thoroughly. Ratios lower than 4:1 were not tested because the suspension did not have enough viscosity to stick to the stainless steel surface. On the other hand, higher than 10:1 suspension was too viscose and made it difficult to produce uniform coating along the Arrow. According to the

251 results shown in Figure 3a, A-ZIF-8/PVC Arrow prepared with 6:1 ratio of ZIF-8 to PVC provided  
252 the highest extraction efficiency to TMA and TEA, and this ratio was used to produce the sorbents.

253 The number of dipping cycles was optimized to provide a maximum thickness of A-ZIF-8/PVC  
254 coating, as higher sorbent volume results in higher extraction capacity to analytes [8] and can also  
255 improve the coating physical stability[31]. The effect of the number of dipping cycles from 1 to 7  
256 was investigated. Over 7 cycles were not tested because the coating became too thick and could not  
257 be withdrawn inside the protective outer tube of the Arrow. As seen from Figure 3b, the extraction  
258 efficiency of amines by A-ZIF-8/PVC Arrow increased from 1 to 5 cycles. From the SEM images  
259 (Figure S2) it was observed that the thickness of A-ZIF-8/PVC coating increased from around 5  $\mu\text{m}$   
260 to 70  $\mu\text{m}$  (from 1 cycle to 5 cycles). After 5 dipping cycles, the extraction efficiency increased only  
261 slightly. Thus, 5 dipping cycles were considered optimal.

### 262 **Figure 3.**

263 To select the optimal aging temperature, both the effect of temperature on the stability of the  
264 coating and minimized leaching impurities from A-ZIF-8/PVC coating during the desorption process  
265 were studied. The tested aging temperatures were 200, 220, 240, 250 and 260  $^{\circ}\text{C}$  in the GC injection  
266 port with constant helium gas flow ( $1.2\text{ mL min}^{-1}$ ) for 1 hour. No large difference in extraction  
267 capability was noticed between different aging temperatures, although 250  $^{\circ}\text{C}$  aging temperature  
268 demonstrated slightly better extraction performance compared to that of 260  $^{\circ}\text{C}$  (Figure 3c). 250  $^{\circ}\text{C}$   
269 gave a relatively clean baseline (data not shown) and was selected as the optimal aging temperature.

### 270 **3.3. The repeatability, reproducibility, physical stability and reusability of ZIF-8 coating**

271 The repeatability of optimized A-ZIF-8/PVC Arrow was investigated. The extraction conditions  
272 were following: 5 mL  $1\text{ }\mu\text{g mL}^{-1}$  TMA solution, 500  $\mu\text{L}$  5M KOH with 2 g NaCl in a 20 mL headspace  
273 vial for 20 min extraction with 1400 rpm agitation, then desorption at 250  $^{\circ}\text{C}$  for 60 seconds. The

274 results showed that relative standard deviation (RSD) for 29 extractions was 10.3% proving a good  
275 repeatability of A-ZIF-8/PVC Arrow for extraction of TMA.

276 The reproducibility of optimally produced A-ZIF-8/PVC Arrow was also investigated. Five  
277 Arrows with the optimized preparation procedure were made in a batch. The extraction and desorption  
278 conditions were same as in the repeatability study with the exception that the extraction solution was  
279 a mixture of TMA and TEA ( $1\ \mu\text{g mL}^{-1}$ ). Triplicate measurements were made with each Arrow.  
280 Satisfactory reproducibility was achieved with 15.6% RSD for TMA and 13.3% RSD for TEA (n=5).

281 The physical stability of optimized A-ZIF-8/PVC Arrow was investigated by comparing the  
282 Arrow before and after conditioning at 250 °C for 28 h. The extraction and desorption conditions  
283 were the same as in the reproducibility study. No noticeable decrease in extraction performance of  
284 A-ZIF-8/PVC Arrow was seen.

285 Reusability of the A-ZIF-8/PVC Arrow was evaluated with repeated extraction cycles of 5 mL  $1\ \mu\text{g mL}^{-1}$   
286 mixture of TMA and TEA. The conditions were the same as in the repeatability study except  
287 for desorption which was 270 °C for 30 seconds. The results are demonstrated in Figure 4. After 130  
288 extraction and desorption cycles, there was no significant decrease in the extraction efficiencies of  
289 both TMA and TEA with A-ZIF-8/PVC coating. The RSD% of TMA was 9.94% and that of TEA  
290 13.03%.

291 **Figure 4.**

### 292 **3.4. Optimization of SPME Arrow conditions**

293 The extraction time optimization for both, A-ZIF-8/PVC Arrow and PDMS/Carboxen-1000  
294 Arrow and the sample volume optimization for A-ZIF-8/PVC Arrow were carried out with a PAL  
295 RTC auto-sampler. Because the minimum extraction temperature in the instrument was 40 °C and  
296 higher temperatures may extract large amounts of water that would affect the peak shapes in GC [8],  
297 40 °C was selected for all the further extractions. The agitation speed was 750 rpm.

### 298 3.4.1. Extraction conditions

299 At first, the KOH concentration was optimized. The concentrations varied from 1 to 10 M and  
300 500  $\mu$ L was used for each sample. Because the peak areas of the analytes increased up to 5 M, it was  
301 selected as the optimal concentration of KOH solution (Figure S3a). The effect of NaCl concentration  
302 on the peak areas of amines was investigated in the concentration range of 0-60% (w/v). The results  
303 (Figure S3b) revealed that the extracted amine amount by A-ZIF-8/PVC Arrow significantly  
304 increased with increasing NaCl concentration until the solution became saturated. Therefore, further  
305 experiments were performed at NaCl concentration of 40%. Three sample volumes 2.5, 5.0 and 7.5  
306 mL were tested in a 20 mL vial with 40% NaCl and 250, 500, and 750  $\mu$ L 5 M KOH solution. The  
307 extraction time in this experiment was 20 min and the incubation time was 10 min at 50  $^{\circ}$ C. According  
308 to the result shown in Figure S3c, the peak areas for both TMA and TEA increased with the sample  
309 volume. So 7.5 mL was chosen as the optimal sample volume for the further experiments. Higher  
310 sample volumes were not tested due to the chance that the sorbent may contact the liquid during  
311 agitation.

312 The extraction time of both A-ZIF-8/PVC and PDMS/Carboxen-1000 Arrows was investigated.  
313 The extraction time of PDMS/Carboxen-1000 was reinvestigated because the extraction temperature  
314 and agitation speed were changed compared to the previous study.[8] The extraction conditions of A-  
315 ZIF-8/PVC Arrow were based on the optimum conditions mentioned above: 7.5 mL TMA and TEA  
316 mixed standard solution in a 20 mL vial, 40% NaCl, and 750  $\mu$ L 5 M KOH solution. Desorption was  
317 performed at 250  $^{\circ}$ C for 60 seconds. The extraction and desorption conditions of PDMS/Carboxen-  
318 1000 Arrow were the same as in section 2.4. The results seen in Figure 5 indicate that the A-ZIF-  
319 8/PVC Arrow reached equilibrium at 5 min, while the PDMS/Carboxen-1000 Arrow at 15 min. The  
320 shorter extraction time achieved by A-ZIF-8/PVC Arrow was mainly due to the thinner coating  
321 thickness of A-ZIF-8/PVC Arrow (70  $\mu$ m) compared to that of PDMS/Carboxen-1000 (120  $\mu$ m)[2].

322 Therefore, in further experiments, the extraction times of 5 minutes were used for A-ZIF-8/PVC  
323 Arrow and 15 minutes for PDMS/Carboxen-1000.

#### 324 **3.4.2. Desorption conditions**

325 Desorption temperature was varied between 205 °C and 270 °C. In order to ensure complete and  
326 fast desorption, 270 °C was chosen. Desorption time of 30 seconds was selected, because it was  
327 enough for complete desorption of analytes.

328 **Figure 5.**

#### 329 **3.5. Method validation**

330 The analytical performance of the A-ZIF-8/PVC Arrow and commercial PDMS/Carboxen-1000  
331 Arrow were investigated under optimal conditions with the PAL auto-sampler pretreatment and GC-  
332 MS analysis. The linear range, limit of quantitation (LOQ) and precision were evaluated for the  
333 extraction of standard TMA and TEA solution. The calibration curves of A-ZIF-8/PVC Arrow for  
334 TMA and TEA were constructed with seven data points with triplicate measurements from 1 ng mL<sup>-1</sup>  
335 to 200 ng mL<sup>-1</sup> and 1 ng mL<sup>-1</sup> to 500 ng mL<sup>-1</sup>, respectively. The correlation coefficient ( $R^2$ ) of TMA  
336 was 0.9903 and that of TEA was 0.9921. The LOQs of TMA and TEA, calculated as three times  
337 standard deviation of the lowest calibration point, were both 1 ng mL<sup>-1</sup>. The linearity of the calibration  
338 was assessed with analysis of residuals and the RSDs of TMA and TEA in the linear range varied  
339 from 2.0 to 24.1% and from 2.6 to 10.1%, respectively.

340 For PDMS/Carboxen-1000 Arrow, the calibration curves were constructed with six data points  
341 from 5 ng mL<sup>-1</sup> to 150 ng mL<sup>-1</sup> for TMA and from 3 ng mL<sup>-1</sup> to 500 ng mL<sup>-1</sup> for TEA, with triplicate  
342 measurements. The calibration was linear and the correlation coefficient was 0.9839 for TMA, and  
343 0.9934 for TEA. The LOQs of TMA and TEA were 5 ng mL<sup>-1</sup> and 3 ng mL<sup>-1</sup>, respectively. The RSDs  
344 of TMA and TEA in the linear range were 3.1-20.3% and 1.9-13.4%, respectively. In general, both  
345 A-ZIF-8/PVC Arrow and PDMS/Carboxen-1000 Arrow performed well with a good linearity and a



346 good repeatability for TMA and TEA analysis. However, A-ZIF-8/PVC Arrow exhibited lower  
347 LOQs with TMA and TEA than PDMS/Carboxen-1000 Arrow. On the other hand, after comparing  
348 the results with already published ones, listed in Table 1, lower LOQs were achieved in this research.

349 A NORDTEST TR 537 procedure [32] was employed for the calculation of the expanded  
350 measurement uncertainty (U) for A-ZIF-8/PVC Arrow approach. U for A-ZIF-8/PVC Arrow was  
351 26% for TMA and 28% for TEA within 95% confidence limit. Compared with the results of our  
352 previous work [8], lower expanded uncertainty was now obtained due to the larger extraction capacity  
353 of the A-ZIF-8/PVC Arrow.

## 354 **Table 1**

### 355 **3.6. Application to wastewater, salmon and mushroom sample analysis**

#### 356 **3.6.1. Wastewater sample**

357 The developed A-ZIF-8/PVC SPME Arrow was applied to the analysis of influent and effluent  
358 wastewater samples under the optimized conditions and the results were then compared with those  
359 achieved by commercial PDMS/Carboxen-1000 SPME Arrow (Table 2 and Figure 6a). Both TMA  
360 and TEA were detected in influent wastewater and their concentrations were  $70.9 \pm 2.8 \text{ ng mL}^{-1}$  and  
361  $270.9 \text{ ng} \pm 20.1 \text{ mL}^{-1}$  by A-ZIF-8/PVC Arrow and  $60.4 \pm 12.9 \text{ ng mL}^{-1}$  and  $228.8 \pm 14.6 \text{ ng mL}^{-1}$  by  
362 PDMS/Carboxen-1000 Arrow, respectively. Only TEA could be detected in effluent wastewater and  
363 its concentration was lower than in the influent wastewater which means that the WWTP purification  
364 process eliminates completely TMA most probably because of its high volatility and TEA only  
365 partially.

366 The influent wastewater was selected for recovery experiments with spiked concentrations because  
367 of its more complex matrix. The recoveries were in the range of 91.6%-92.1% and the RSDs for the  
368 three replicate sampling were 7.0%-7.4%. Higher recovery of TEA and smaller RSDs were obtained  
369 by A-ZIF-8/PVC Arrow compared to those obtained by PDMS/Carboxen-1000 Arrow. This may be

370 due to the large pore size of acidified ZIF-8 material (about 50 nm) being more suitable for larger  
371 molecular size TEA (8.4 Å). On the other hand, the pore size of Carboxen-1000 material was smaller  
372 than 8.0 Å, being worse for TEA extraction. Furthermore, both SPME Arrows exhibited the similar  
373 recoveries to TMA due to its smaller molecular size, 5.6 Å, compared to TEA. In summary, A-ZIF-  
374 8/PVC Arrow showed better extraction capability than PDMS/Carboxen-1000 Arrow for TMA and  
375 TEA.

### 376 3.6.2. Salmon sample

377 A-ZIF-8/PVC SPME Arrow and commercial PDMS/Carboxen-1000 SPME Arrow were also  
378 utilized for monitoring freshness of salmon by detecting TMA and TEA concentration, which are the  
379 indicators of spoilage.[33] The changes of TMA content in salmon stored at room temperature are  
380 shown in Figure S4 and the chromatograms in Figure 6b. Only TMA could be detected in salmon  
381 samples. The initial concentration of TMA was  $0.020 \pm 0.003$  and  $0.014 \pm 0.008$  mg/100 g, as  
382 determined by A-ZIF-8/PVC Arrow and PDMS/Carboxen-1000 Arrow, respectively. After three days  
383 of storage, the TMA values largely increased up to  $3.58 \pm 0.389$  mg/100 g (determined by A-ZIF-  
384 8/PVC Arrow) and  $2.99 \pm 0.935$  mg/100 g (determined by PDMS/Carboxen-1000 Arrow). The A-ZIF-  
385 8/PVC Arrow showed similar results for the amount of extracted TMA than PDMS/Carboxen-1000  
386 Arrow when taking standard deviations into account. In addition, A-ZIF-8/PVC Arrow gave lower  
387 standard deviation compared to PDMS/Carboxen-1000 in the complex fish sample. The values and  
388 curve of TMA content increase with storage time in salmon samples were comparable to results  
389 reported earlier [34-36] and the reason for a slightly higher concentration detected in this study may  
390 be due to the higher storage temperature used.

### 391 3.6.3. Mushroom analysis

392 As can be seen in Figure S5, only TMA could be detected in mushroom samples, and with the ZIF-  
393 8/PVC Arrow TMA could be detected in the all four samples (#1, #2, #3 and #4) while commercial

394 PDMS/Carboxen-1000 Arrow could detect TMA only in three samples (#2, #3 and #4), and the peak  
395 intensity of TMA extracted by ZIF-8/PVC Arrow was regularly higher than that extracted by  
396 PDMS/Carboxen-1000 Arrow.

397 **Figure 6.**

398 **Table 2**

399

## 400    **Conclusions**

401        In this study, we demonstrated the applicability of ZIF-based material as SPME Arrow sorbent for  
402        the determination of small volatile amines in different sample matrices. A simple physical adhesion  
403        approach was employed for the fabrication of hydrophobic ZIF-8 material as sorbent for SPME  
404        Arrow. The pore size of ZIF-8 adsorbent was modified by headspace acidification and then used for  
405        extraction of volatile low molecular weight alkylamines. The fabricated A-ZIF-8 SPME Arrow was  
406        highly efficient, reusable and reproducible. Its potential application as SPME Arrow adsorbent was  
407        proved by the extraction of trace level amines in wastewater, salmon and mushroom samples prior to  
408        GC/MS analysis and the results were comparable with those achieved by commercial  
409        PDMS/Carboxen-1000 SPME Arrow. A-ZIF-8/PVC Arrow provided acceptable flexibility for TMA  
410        and TEA extraction in practical applications due to larger pore size of acidified ZIF-8. In addition,  
411        ZIF-8 based Arrow-GC/MS method exhibited lower limit of detections compared with those of  
412        Carboxen-1000 based Arrow-GC-MS method. Furthermore, ZIF-8-coated SPME Arrow showed  
413        satisfactory selectivity for amines in complex mixtures. Considering the porosity and modifiable  
414        structure, good physicochemical properties and large surface area, the ZIF-based MOF material is  
415        promising as adsorbent for SPME Arrow for the extraction of short chain aliphatic amines.

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538 **Figure captions**

539 Figure 1. Schematic of the fabrication of Acidified-ZIF-8/PVC SPME Arrow.

540 Figure 2. Extraction performance for trimethylamine, (a) pure ZIF-8 Arrow, acidified pure ZIF-8  
541 Arrow and PDMS/Carboxen-1000 Arrow, (b) ZIF-8/PVC Arrow and acidified–ZIF-8/PVC Arrow. 5  
542 mL of 1  $\mu\text{g mL}^{-1}$  TMA solution for 20 minutes extraction, and desorption at 250 °C for 60 seconds.

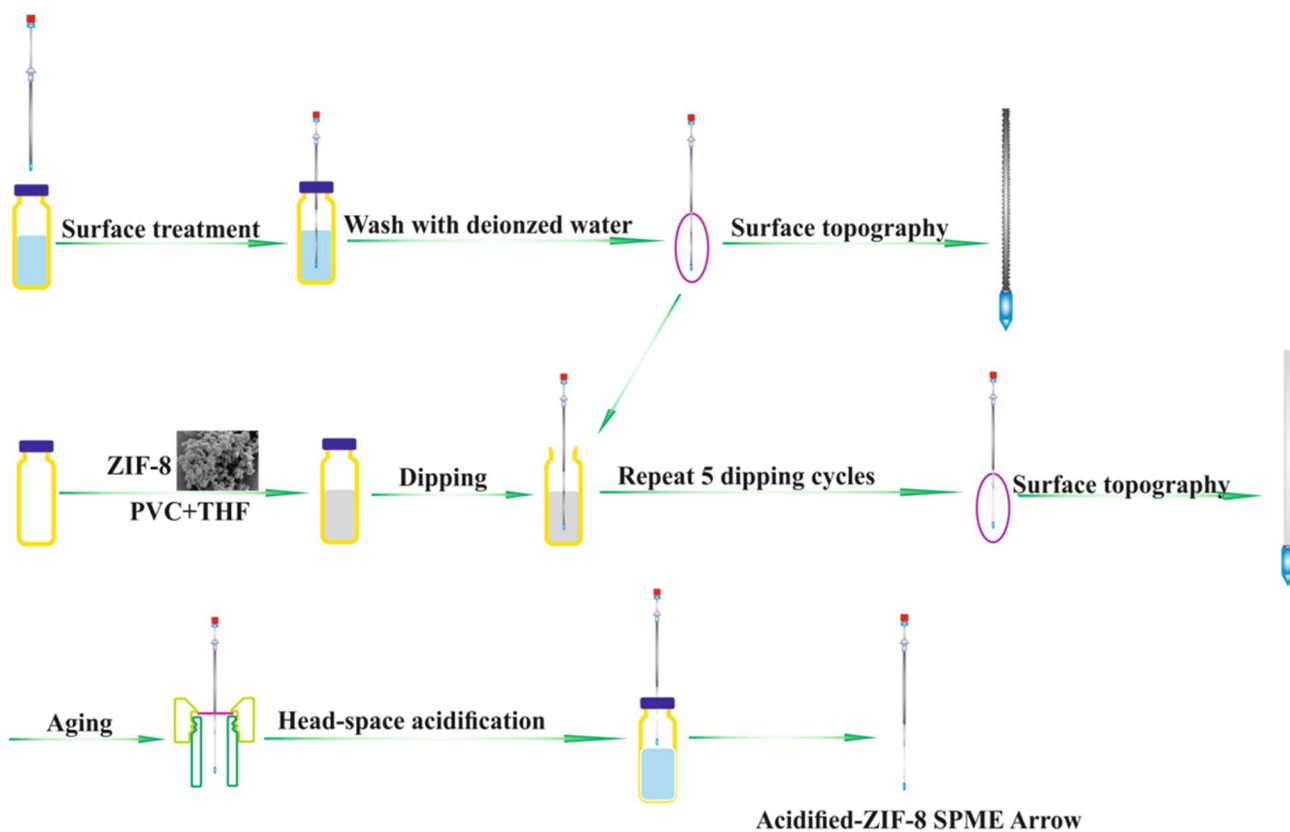
543 Figure 3. Acidified ZIF-8/PVC coating preparation optimization, (a) ZIF-8:PVC ratio optimization,  
544 (b) dipping cycle optimization and (c) aging temperature optimization. 5 mL of 1  $\mu\text{g mL}^{-1}$  TMA  
545 solution for 20 minutes extraction and desorption at 250 °C for 60 seconds.

546 Figure 4. Reusability of acidified-ZIF-8/PVC SPME Arrow. Relative adsorption definition: the peak  
547 area of second extraction was set as 100% and the relative peak area of other extractions were  
548 determined by division of the peak area by the second extraction peak area  $\times 100$ .

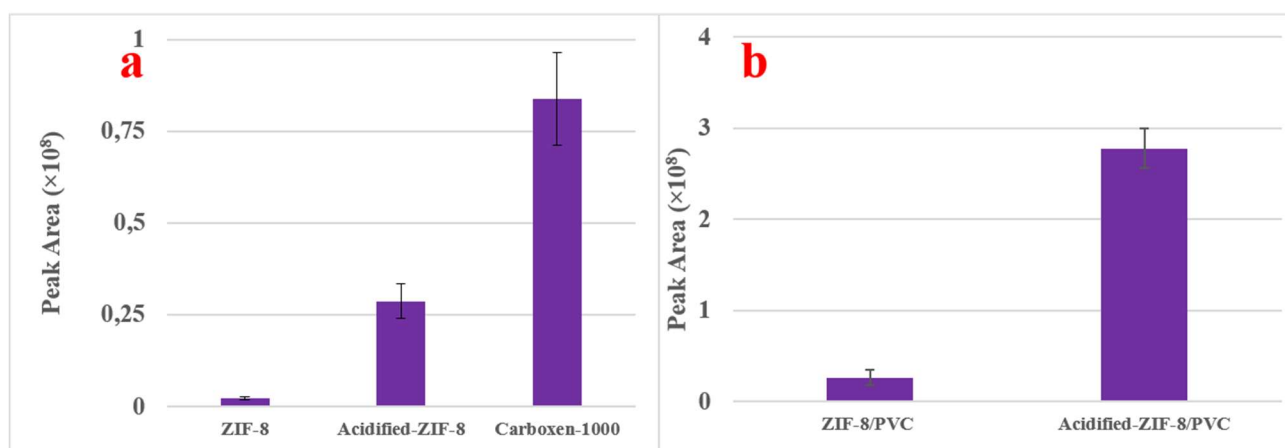
549 Figure 5. Extraction time profiles with acidified-ZIF-8/PVC (a) and PDMS/Carboxen-1000 (b) SPME  
550 Arrows.

551 Figure 6. GC-MS chromatograms of influent wastewater sample (A) and salmon sample (B) after  
552 extraction with A-ZIF-8/PVC SPME Arrow (purple) and PDMS/Carboxen-1000 SPME Arrow  
553 (black).

554

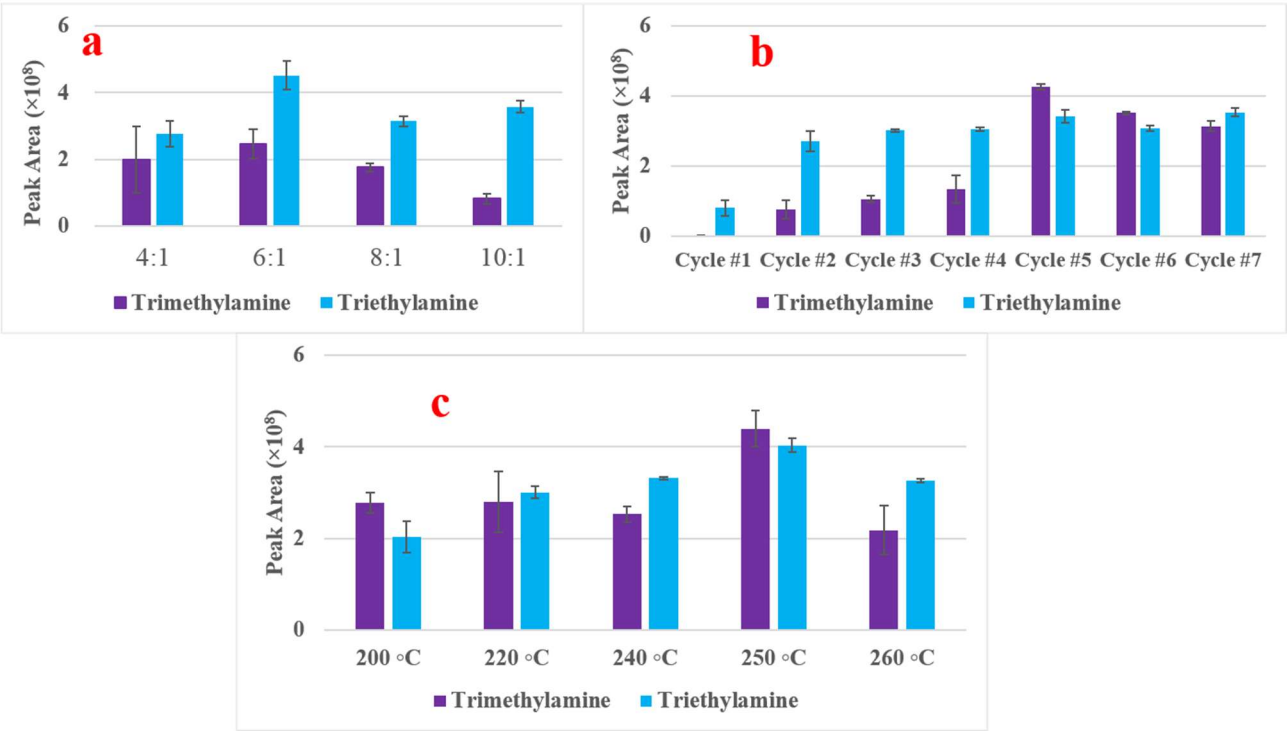


**Figure 1.**



**Figure 2.**

562

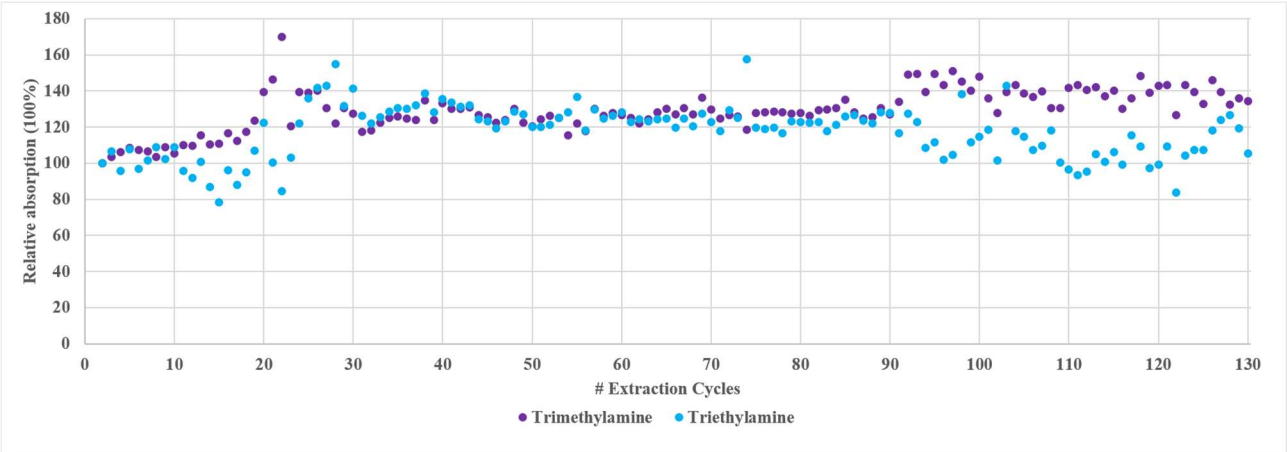


563

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565 **Figure 3.**

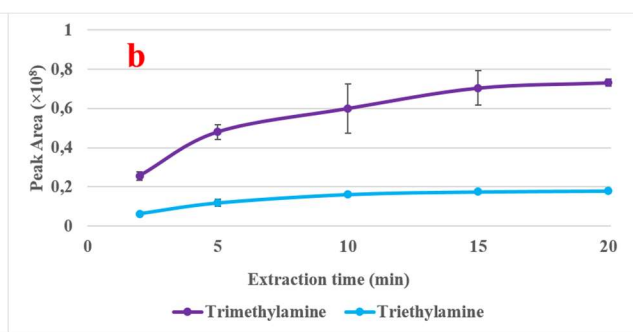
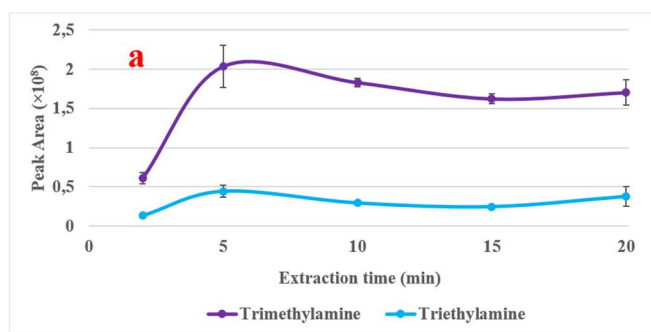
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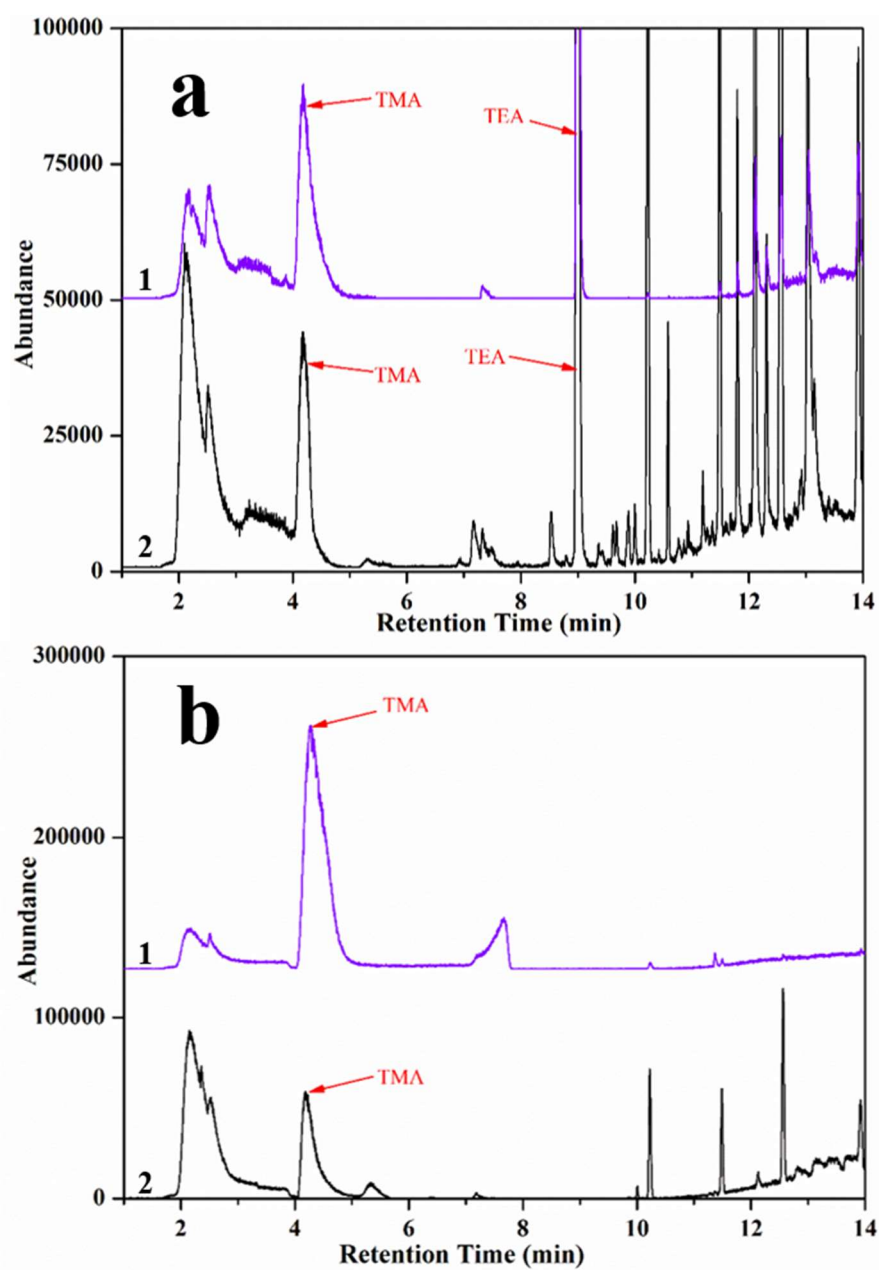
567

568 **Figure 4.**

569



**Figure 5.**



**Figure 6.**

581 **Table 1**

582 Comparison with other sampling methods for the determination of TMA and TEA.

Technique	Matrix	LOQ (ng mL <sup>-1</sup> )	Linear range (ng mL <sup>-1</sup> )	RSD(%)	Reference
Carboxen/PDMS-SPME-GC-MS	Gas standard	2.38 ppbv (MDL <sup>a</sup> , TMA)	~3.2-210 ppbv (TMA)	Not provided	[15]
PDMS-SPME-GC-NPD	Wastewater and	11 (LOD <sup>b</sup> , TMA)	47-563 (TMA)	16 (TMA)	[37]
	Sewage-Polluted Water	14 (LOD, TEA)	60-714 (TEA)	14 (TEA)	
PDMS/DVB-SPME-GC-FID	Air	0.55 mg m <sup>3</sup> (TMA)	Not provided	Not provided	[38]
		0.86 mg m <sup>3</sup> (TEA)			
Amide bridged-C-SPME-GC-FID	Fish tissue	25.89 (LOD, TMA)	500-80000 (TMA)	5.1 (TMA)	[39]
		7.37 (LOD, TEA)	50-5000 (TEA)	1.4 (TEA)	
PDMS/DVB-SPME-GC-MS	Vegetables	58 (TMA)	Not provided	9.2 (TMA)	[40]
Carboxen/PDMS-SPME-GC-MS	Urine	14.9 µmol L <sup>-1</sup> (TMA)	14.9-956 µmol L <sup>-1</sup> (TMA)	12.2 (TMA)	[41]
PDMS-SPME-GC-FID	Standard TMA	0.04-0.8 mg (TMA)	2980 ng (MDL, TMA)	10 (TMA)	[42]
This article	Wasterwater	1 (TMA)	1-200 (TMA)	2.0-24.1 (TMA)	
	Salmon	1 (TEA)	1-500 (TEA)	2.6-10.1 (TEA)	
	Mushroom				

583 <sup>a</sup> Method detection of limit.

584 <sup>b</sup> Limit of detection

585

586 **Table 2**

587 Comparison of A-ZIF-8-SPME Arrow and PDMS/Carboxen-1000 SPME Arrow for the extraction  
588 and GC-MS analysis of wastewater.

Analytes	A-ZIF-8 SPME Arrow				PDMS/Carboxen-1000 SPME Arrow			
	Concentration		Recovery		Concentration		Recovery	
	(ng mL <sup>-1</sup> ) <sup>a</sup>		RSD		(ng mL <sup>-1</sup> ) <sup>a</sup>		RSD	
	Effluent	Influent	Influent		Effluent	Influent	Influent	
	wastewater	wastewater	wastewater <sup>b</sup>		wastewater	wastewater	wastewater <sup>b</sup>	
Trimethylamin	Not detected	68.4±5.3	92.1	7.0	Not detected	62.2±7.8	91.6	7.4
Triethylamine	70.9±2.8	270.9±20.1	91.6	7.4	60.4±12.9	228.8±14.6	73.9	14.4

589 <sup>a</sup> Wastewater sample without spiking.

590 <sup>b</sup> Spiked with 100 ng mL<sup>-1</sup> trimethylamine and 200 ng mL<sup>-1</sup> triethylamine.